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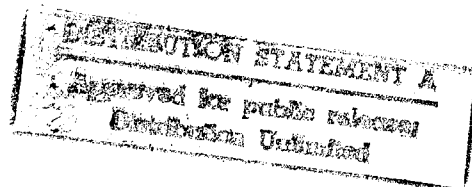
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INVESTIGATIONS OF THE ION EXCHANGE
RESINS IN USE IN SOUTH AFRICA

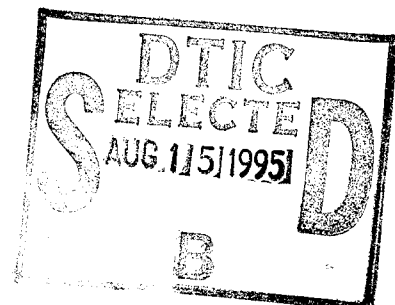
Topical Report

By
Sallie A. Fisher

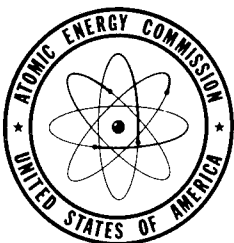


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TOPICAL REPORT RMO-2510

INVESTIGATIONS OF THE ION EXCHANGE
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By

Sallie A. Fisher

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A B S T R A C T

An investigation of the "poisoned" Compound A and Amberlite IRA-400 in use at Western Reefs, South Africa indicates that silica is the principal cause of the sudden losses of uranium capacity. Regeneration with sodium sulfide has restored relatively new Compound A and IRA-400 to their original capacities but old IRA-400 has only 75 per cent of its original capacity after this treatment. Periodic alkaline regeneration to remove accumulated silica is recommended.

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TOPICAL REPORT

INVESTIGATION OF THE ION EXCHANGE RESINS IN USE IN SOUTH AFRICA

By

Sallie A. Fisher

INTRODUCTION

In August, 1951 the operators of the plant at Western Reefs first experienced what they term a "poisoning" of the Amberlite IRA-400 then in use at that installation. As a result of this "poisoning" the uranium capacity of the resin decreased markedly. The resin in use at that time was subsequently regenerated and restored to use. On July 8, 1952, a similar "poisoning" of both the Amberlite IRA-400 and Compound A occurred. Samples of these resins, both in the "poisoned" and in the regenerated state were shipped to this laboratory for investigation of the mode and extent of "poisoning" and of the effectiveness of the regeneration.

OBJECT OF INVESTIGATION

The investigation of the "poisoned" samples of Amberlite IRA-400 and Compound A from Western Reefs was threefold in scope:

1. Determination of the total anion exchange capacity and of the quaternary ammonium exchange capacity of the resins as received.
2. Comparison of the uranium capacity (column loading and elution) with fresh samples of Amberlite IRA-400 and Compound A.
3. Determination of the amount and character of the ash present in the samples as received.

By combining the results of the three approaches a reasonably complete conclusion as to the nature of the poisoning and the means for correcting and/or preventing it can be drawn.

SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

Examination of the "poisoned" samples of Compound A and Amberlite IRA-400 from the Western Reefs installation has indicated that these resins have suffered marked apparent loss of quaternary ammonium capacity and of uranium

capacity. The poisoned samples were all found to contain abnormal amounts of silicious material in addition to small amounts of uranium and other metallic constituents.

Regeneration of the samples with sodium sulfide has effectively removed the major portion of the silica from the "poisoned" resins but has had little effect on the amount of metallic ash. This regeneration has succeeded in restoring Compound A to its original state, as confirmed by quaternary ammonium capacity and uranium capacity data. Restoration of the Amberlite IRA-400 is less complete and is less successful with "old" resin than with the newer batches. The Amberlite IRA-400 that has been in use for somewhat more than one year is 25-30% lower in both quaternary and uranium capacity even after the sodium sulfide regeneration. It also shows an increased nitrogen and ash content. If this value is corrected for the gain in porosity as noted by the gain in moisture, the actual loss in capacity (both quaternary and uranium) is but 20 per cent after more than one year's operation. From the evidence at hand it is felt that the most likely explanation of the sudden "poisoning" is the precipitation (or coagulation) of silicic acid in the resin structure which blocks off the exchange groups. This can be most effectively avoided by a periodic alkaline regeneration (every 10-15 cycles) to remove the silica which has built up in the resin during repeated acid cycles. In addition, noticeable amounts of sulfur are also present and may contribute to temporary loss in uranium loading. Sodium sulfide removes the sulfur contamination.

The loss of capacity of "old" Amberlite IRA-400 even after sodium sulfide regeneration is apparently not due to a single cause. From the data thus far accumulated the slow buildup of metallic ash (which appears to have cobalt as a major constituent), the increase in nitrogenous material probably in the form of complex anions, and the conversion of quaternary groups to less basic nitrogen containing groups all may contribute to the observed result. Further work is planned to obtain a clearer picture of the behavior of Amberlite IRA-400 after prolonged use in the nitrate cycle as there is an indication that the porosity and hence the sharpness of the elution peak is increasing with use.

It has also been concluded that the residual capacity (80% of the original) of the Amberlite IRA-400 that has been in operation for over a year has an elution efficiency superior to that of the original resin for 70 per cent elution. This, of course, is only after the rejuvenation treatment. For 100 per cent uranium elution, the elution efficiency is approximately the same.

Microscopic examination of the resins indicate no marked physical break-down in the resin after a year's operation.

Experiment Procedures and ResultsThe Samples

Seven samples were received from the Western Reefs installation. These are designated as follows:

- A-1 Compound A Poisoned. In nitrate form.
- A-2 Compound A Poisoned and then regenerated. In nitrate form.
- B-1 New Amberlite IRA-400. Poisoned. In nitrate form.
- B-2 New Amberlite IRA-400. Poisoned and then regenerated. In nitrate form.
- C-1 Old Amberlite IRA-400; originally poisoned and regenerated in August 1951. Repoisoned July 8, 1952. In nitrate form.
- C-2 Old Amberlite IRA-400; originally poisoned and regenerated in August 1951. Repoisoned July 8, 1952. Regenerated and restored to nitrate form.
- D Sludge backwashed from Sample C-1 during the regeneration process.

To give a more comprehensive picture of the past history of the samples we quote from a letter (July 25, 1952) from Mr. M. G. Atmore of the Transvaal Chamber of Mines:

"The conditions under which the resins were operated are very similar to those which existed when they last failed, in that the resin had been stored for some three days in the nitrate form and the pregnant solution was in all probability not fresh.

"The regeneration treatment used was, unfortunately, not the complete cycle which I recommended, and consisted only in treating the material with 5% sodium sulphide for 24 hours, followed by cold water wash and treatment with 15% nitric acid.

"I also suspect that insufficient washing was carried out, - - - -."

Determination of Total Exchange Capacity and of the Quaternary Capacity

The six resin samples as received were evaluated to determine the quaternary ammonium exchange capacity and the total anion exchange capacity using our standard control methods.¹ Results (Table 1) from the resins are given first on a dry weight as received (nitrate form) and have then been recalculated to correct to the hydroxide form of the resin. Further corrections for the ash content, both in the nitrate and in the hydroxide forms are given. It should be emphasized that while all these results represent the capacity determinations as received, it is possible that a certain amount of further regeneration has occurred in the process of determining the total anion and quaternary capacities as the first step in such procedures involves the treatment of the sample with 4% sodium hydroxide. The series of results headed "After NaOH regeneration" represent the capacities obtained by weighing the sample as received and then soaking it in 4% sodium hydroxide that had been warmed to 45°C. With the exception of this step the quaternary and total anion capacities were determined by the same method as was used on the original sample. The per cent nitrogen was determined in the samples that had already been cycled through the total anion capacity and quaternary capacity determinations and converted back to their hydroxide form. The average value obtained in routine production control of these resins is given at the bottom of the table.

From the results given in Table 1 it is immediately obvious that the "poisoned" resins (A, B & C-1) have suffered a marked apparent loss in quaternary capacity. This loss in capacity is still evident after the results have been corrected for their nitrate and ash contents and in the case of the IRA-400 is more noticeable in the older resin.

The regeneration procedure used at Western Reefs has resulted in an improvement in quaternary capacity in all cases, but has not restored the quaternary capacity to a value equal to that of the original resin, even when a correction for ash is made. These low values for quaternary capacity might be due either to a still incomplete regeneration or to an actual loss of quaternary groups. In the latter case the mechanism might be either a complete loss of nitrogen or a conversion of the quaternarized nitrogen into some less basic amino group. A careful analysis of results in Table 1 indicated that the low quaternary capacity is due to both incomplete regeneration and to a loss of quaternary nitrogen.

¹. The quaternary anion exchange capacity is determined by converting the resin to the free base form with 4% sodium hydroxide, washing with water and subsequently exchanging sulfate ions for the hydroxide ions associated with quaternary ammonium groups in the resin and titrating the hydroxide ions thus liberated. The total anion exchange capacity is determined by converting all amine groups to their chlorides or hydrochloride with 4% hydrochloric acid rinsing with alcohol and subsequently eluting the chloride with 4% sodium sulfate and measuring the amount of chloride thus eluted.

TABLE I.

Exchange Capacities of Western Reef's Resins

Sample	A-1	A-2	B-1	B-2	C-1	C-2
As submitted-nitrate form						
Total Anion Capacity	2.40 meq./g.dry	2.71	2.85	3.08	2.24	2.36
Quaternary Capacity	1.63 meq./g.dry	2.20	1.74	2.10	1.08	1.53
Corrected to hydroxide form						
Total Anion Capacity	2.73 meq./g.dry	3.13	3.35	3.64	2.55	2.65
Quaternary Capacity	1.85 meq./g.dry	2.54	2.04	2.49	1.17	1.72
As submitted corrected for ash						
Total Anion Capacity	2.65 meq./g.dry	2.78	2.98	3.11	2.45	2.45
Quaternary Capacity	1.80 meq./g.dry	2.25	1.82	2.12	1.17	1.58
Hydroxide form corrected for ash						
Total Anion Capacity	3.01 meq./g.dry	3.20	3.51	3.68	2.77	2.74
Quaternary Capacity	2.05 meq./g.dry	2.60	2.14	2.51	1.27	1.78
After NaOH Regeneration						
Quaternary Capacity- Nitrate form		2.53		2.29		1.92
Quaternary Capacity- OH form-corrected for ash		2.99		2.73		2.23
Total Anion Capacity- Nitrate form		2.85		2.95		2.36
Total Anion Capacity- OH form-corrected for ash		3.35		3.53		2.74
% Ash - As Submitted	9.36	2.38	4.44	1.02	8.06	3.33
% Nitrogen-hydroxide form	5.2	4.4	5.5	5.4	6.2	6.2
Total Anion Capacity Calc. from % N.	3.7	3.1	3.9	3.8	4.4	4.4
Average Total Anion Cap. Fresh Resin (OH form)		3.40		3.60		3.60
Average Quaternary Cap. Fresh Resin (OH form)		2.95		3.15		3.15

RMO-2510-5

Evidence of the incomplete regeneration is to be found in the promising increase in quaternary capacity after a single laboratory treatment with warm (45°C) 4% sodium hydroxide. Compound A appears to be completely restored to its original condition by this treatment while the quaternary capacity of IRA-400 has increased by a tangible, though less spectacular, percentage. However, a comparison of the "new" IRA-400 (B-2) and the "old" IRA-400 suggests the probability of a loss of quaternary groups with time. That this probable loss of quaternary has occurred without loss of nitrogen is evident from the results of the nitrogen determinations by the Kjeldahl method. Not only is all the original nitrogen (Range 4.5 to 5.0%) present but the nitrogen content of the IRA-400 is increasing. The magnitude of this increase cannot be accounted for by dequaternization (which presumably would be accompanied by some loss in equivalent weight) alone and hence must be at least partially due to the build-up of nitrogen containing complexes (as, for example, cobalt thiocyanates or cyanides) in the resin. Regeneration, as carried out at Western Reefs, does not seem to have removed these complexes from IRA-400 but has lowered the nitrogen content of Compound A to a value that agrees closely with the total anion exchange capacity of the sample. In the absence of conclusive evidence proving either loss of quaternary capacity by dequaternization or by "blocking" of the quaternary groups with nitrogen containing complex ions it is presumed that both mechanisms contribute to give the observed results.

Comparison of the Uranium Capacity of the Western Reefs Samples with that of Fresh IRA-400 and Compound A

The column behavior of the resins received from Western Reefs were determined in the sulfate-chloride cycle so that the results could be compared with the corresponding data from fresh IRA-400 and Compound A already available in this laboratory. For this purpose twenty milliliter beds in a standard 50 ml. buret were regenerated with 5% sulfuric acid and then rinsed free of excess acid with water. Uranium (VI) sulfate solution containing 1 g./liter uranium and having a pH of 2 was passed through the bed at the rate of 1 gal./ft.³-min. The capacity is calculated in milligrams uranium/ml. of resin using a 10% leakage as the breakthrough point. Results are given in Table 2. Also given for references are the percentage of the original uranium capacity attained and of the original quaternary capacity, these percentages based on the capacities of typical fresh Compound A and IRA-400.

TABLE 2

Uranium Loading of Western Reefs Samples

Sample	Mg. U/ml. resin	% Normal U Cap.	% Normal Quat. Cap.
A-1	37	65	69
A-2	57	100	88
B-1	51	64	68
B-2	74	94	80
C-1	27	34	40
C-2	58	72	56
C-2*	55	69	71
New Compound A	57		
New IRA-400	80		

* After regeneration with 4% NaOH at 45°C

From Table 2 it may be seen that the "poisoned" samples (A, B & C-1) have lost a significant portion of their uranium capacity and that the percentage loss in uranium capacity is almost identical with the percentage loss in quaternary capacity. The regeneration procedure in use at Western Reefs has restored the uranium capacity of samples A and B to greater than 90% of the original. Sample C, the IRA-400 that has been in use since early summer 1951 and which showed serious loss both in uranium and quaternary capacity, has been less completely restored to its original capacity by the Western Reefs regeneration. Additional regeneration with 45°C sodium hydroxide improved the quaternary capacity but did not increase the uranium capacity of sample C.

Leakage of uranium during the run was less than 0.01 mg./ml. of effluent in all cases. The breakthrough characteristics of the South African samples were the same as those of fresh resin: sharp with a rapid increase in leakage in the case of the Compound A samples and slowly with a gradual increase in leakage when the IRA-400 samples were tested.

Elution of the columns loaded with uranium in the sulfate cycle was carried out with approximately 0.9N NaCl - 0.1N HCl solution at the rate of 1 gal./ft.³-min. Elution curves are shown in Figures 1 and 2. The plots given there have been calculated to eliminate variations in the bed volumes and the loading of the resins studied. The abscissa is obtained by dividing the total volume of effluent (milliliters) by the milliliters of resin in the bed. The ordinate scale represents the concentration of uranium found in the effluent (mg./ml.) divided by the loading of the column expressed in mg. uranium/ml. resin.

In the case of Compound A (Figure 1) the "poisoned" resin sample, A-1, was less efficiently eluted than fresh Compound A. This resin after regeneration, sample A-2, was so similar to fresh Compound A that a single elution curve could be drawn from the results of the two elutions. Thus Sample A-2 appears to be satisfactorily restored to its original state in all respects by the Western Reefs regeneration process.

The elution curves of all four samples of IRA-400 from Western Reefs were strikingly similar; so similar that they fall on a single curve (Fig. 2). However, the shape of this curve is quite different from that obtained with fresh IRA-400 and much closer in shape to that of fresh Compound A. This would indicate that the elution characteristics of IRA-400 tend to improve after usage in this application, this improvement probably resulting from an increase in porosity following some irreversible swelling. An independent check on the change in the porosity of a resin may be obtained by determining its moisture content. The IRA-400 from Western Reefs was found to contain slightly more than 50% moisture as compared with a 40-45% water content in fresh material, thus confirming an increase in porosity with use.

This observed sharpening of the elution band of IRA-400 prompted a re-check of the per cent uranium recovered as a function of the volume of eluting used. Integration of the area under the curves in Figures 1 and 2 resulted in the percentage recovery curve in Figure 3. From this it may be seen that Compound A retains its advantage in the percentage uranium eluted per bed volume of eluting agent. At low volumes of eluting agent the IRA-400 from Western Reefs is more rapidly eluted than fresh IRA-400, but this advantage is lost if more complete elution per cycle is desired. Of perhaps greater economic interest is the amount of uranium recoverable per volume of eluting agent. Figure 4 is a plot of this nature comparing the Western Reefs samples with fresh resin. Here again Compound A and Sample B-2 have an advantage over fresh IRA-400 at low volumes of eluting agent. If larger volumes of eluting agent are used the resin with the highest loading naturally gives the greatest uranium return.

Determination of the Ash Content of Western Reefs Resins

In an effort to obtain some clue as to the nature and extent of the "poisoning" material a brief analysis of the ash content of the resins as received from Western Reefs was conducted. This analysis consisted first of the determination of the total ash formed on treatment of the resin with concentrated sulfuric acid followed by an ignition at 900°C. The silica content of this ignited ash was then determined by acid leach, dehydration and subsequently by hydrofluoric acid treatment of the filtered and ignited residue. Finally a fluorimetric uranium analysis of the filtrate from the acid leached ash was conducted. Results of these analysis are given in Table 3. All percentages are based on the dry weight of the resin in the nitrate form (as received).

The average ash content of fresh IRA-400 and of Compound A is below 0.5%. Thus all the samples contain ash far in excess of the normal amount. A breakdown of the ash into silicious and non-silicious ash indicates that a large fraction of the ash (note that all percentages given are based on total weight of resin, not total weight of ash) in the "poisoned" samples is silicious. This portion of the ash is quite effectively removed by the regeneration technique in use at Western Reefs and undoubtedly could be as completely removed from sample A-2 and C-2 as it has been from B-2 by a repetition of the regeneration procedure.

TABLE 3

Ash Content of the Western Reefs Samples

Sample	Total % Ash	% SiO ₂	% U as U ₃ O ₈	% Non-silica and Non-U Ash
A-1	9.36	7.63	0.23	1.50
A-2	2.38	1.16	0.073	1.15
B-1	4.44	3.45	0.043	0.95
B-2	1.02	0.18	0.027	0.81
C-1	8.06	5.72	0.23	2.11
C-2	3.33	1.32	0.19	1.82

In addition to the silicious fraction the "poisoned" resin contains a small percentage of uranium. This content is also diminished during the regeneration and is low enough thereafter to be considered a negligible source of trouble.

More serious, from a capacity standpoint, is the gradual buildup of non-silicious, non-uranium ash. Comparison of the B samples with the C samples shows that this ash is building up with time and further that the present regeneration procedure removes only a small portion of this ash. A detailed analysis of this fraction was not carried out but the presence of cobalt was obvious from the color of the various residues and solutions.

A similar analysis of the sludge backwashed from sample C-1 was conducted. Inspection of this sludge showed it to be a grayish mud containing some whole resin beads. This sludge was first dried at 110°C and all subsequent analyses reported in Table 4 are expressed as percentages of the dried sludge unless otherwise noted.

TABLE 4

Analysis of the Sludge Removed from Sample C-1

	Sample I	Sample II
Loss on ignition 900°C	52.6%	52.9%
% Silicious Material	20.4%	19.9%
% U_3O_8	4.6%	3.2%
% SiO_2 in Ignited Ash	43.0%	42.3%

A more detailed analysis of this sludge is expected from the Watertown Arsenal group. This preliminary work does indicate that the sludge is high in silica and in material volatilized on ignition.

In addition to the large quantities of silica and metallic complexes that are built up on the resin, large quantities of colloidal sulfur are apparent in the "poisoned" resin samples. The sodium sulfide treatment removes this contamination quite effectively.

Operational Recommendations

An overall analysis of the resins that have been in operation in South Africa for at least three months, and in one case for at least one year, is quite encouraging. Three months operation does not show any resin degradation. Therefore any loss of uranium capacity is due to mechanical blocking with colloidal silica and colloidal sulfur. This blocking may occur gradually or build up suddenly if the resin is permitted to stand idle in the nitrate-nitric acid state after elution. This loss in uranium loading can be readily recovered by treatment with sodium sulfide and caustic.

After one year's operation, the IRA-400 exhibits signs of some resin degradation. Eighty per cent of the uranium operating capacity originally present can be recovered by the sulfide treatment; however, the remaining twenty per cent decrease is due to a loss in quaternary nitrogen and/or irreversible binding of some metallic complexes such as cobalt thiocyanates or cyanides.

In view of these findings, the following operational precautions should be considered:

1. The resins should be treated with moderate (10-20%) concentrations of sodium sulfide or caustic more frequently in order to prevent the build-up of aged colloidal silica and sulfur. Although this may be expensive, recycle of at least a portion of this solution should be possible.

2. The resins should not remain idle for long periods in the nitrate form or in the presence of a strong acid unless the silica has been removed.

Figure 1

Elution of Compound A with Sodium
Chloride-Hydrochloric Acid Solutions

x = Fresh Compound A

o = Sample A-2

⊕ = Sample A-1

$\frac{C_s}{C_{R_0}}$ = $\frac{\text{Mg. U/ml. eluent}}{\text{Mg. U/ml. resin}}$

$\frac{C_s}{C_{R_0}}$ = $\frac{\text{Mg. U/ml. resin}}{\text{Mg. U/ml. resin}}$

